THE MOTION OF ELECTRONS IN CARBON MONOXIDE

By H. B. Wahlin

Abstract

Motion of electrons in carbon monoxide.—*Formation of negative CO ions* was found, in previous mobility experiments, to be extremely rare. This result has now been verified with CO generated by formic acid dripping into concentrated sulphuric acid and purified with great care. The very high mobilities obtained indicate clearly that an electron liberated in pure CO remains free. *Electron mobility as a function of field and pressure* was studied using alternating potentials with frequencies up to 340,000 cycles, generated by a vacuum tube oscillating circuit. At a pressure of 723 mm a mobility of 118 m/sec/volt/cm was measured, which decreased to 81.5 m as the field intensity increased from 4.5 to 48 volts/cm. The Townsend-Compton theory of mobility leads to the following equation for the speed of an electron in a field x: $v = a(x/p)/\sqrt{B + (x/p)}$. This leads to a relation between frequency and critical value of the field X_1 which is found to agree with the results for CO if $a = 1.87\ (10)^6$ and $B = .005$, the pressure being in mm Hg. This agreement suggests (1) that the mean free path is independent of the field, and (2) that the electron collisions with CO molecules are very inelastic.

In an earlier article[1] measurements of mobilities were reported which showed that only rarely does an electron attach itself to a molecule of carbon monoxide. In fact, it was found that on the average, the electrons make 10^8 impacts before uniting to form a negative ion, and mobilities as high as 240 cm/sec/volt/cm were obtained at atmospheric pressure.

In a determination of this kind, however, the presence in the gas of a small amount of impurity could alter the results appreciably, especially if the impurity were of an electronegative character, because the electrons show a greater tendency to unite with electronegative substances than with others. It was necessary, therefore, that extreme precautions be taken in generating and purifying the gas, not only to eliminate impurities as far as possible, but also to limit the kinds of impurities which could possibly be present. It was in order to determine whether, when a different method was used in generating the carbon monoxide, results differing from those given above would be obtained, that the following experiments were undertaken.

In the previous work, the carbon monoxide was generated through the action of concentrated sulphuric acid on sodium-formate. This method

---

[1] H. B. Wahlin, Phys. Rev. **19**, p. 173 (1922).

was found to be unsatisfactory, however, due to the fact that the evolution of gas was difficult to control. In these later experiments formic acid was substituted for the sodium-formate. The formic acid was allowed to drip into the concentrated sulphuric acid and by varying the rate of drip, the rate of evolution of the gas could be controlled at will.

From the generator the gas passed through a solution of potassium hydroxide to remove any sulphur dioxide and sulphur trioxide fumes which might be given off from the sulphuric acid during the reaction. This would also remove any formic acid vapors that might be carried over. Next the gas passed over calcium chloride to dry it partially and then through a tube containing hot copper which had first been reduced by hydrogen. At this stage any oxygen present in the gas would unite with the carbon monoxide molecules to form carbon dioxide. In order to remove this, the gas passed through a tower about 75 cm high, containing glass beads and a solution of potassium hydroxide. The glass beads served to break up the bubbles of gas and to retard their progress through the solution. The gas next passed through a tube about 75 cm long, containing solid potassium hydroxide, and then through a similar tube containing calcium chloride. It next passed over phosphorous pentoxide to complete the drying, through a trap and a spiral both cooled to liquid air temperature, and into the chamber in which the measurements were made. The gas was generated as slowly as possible so that its passage through the purification system took some time. In making a filling, the chamber was washed out by exhausting to a pressure of 1 mm of mercury or less and filling it to atmospheric pressure. This was repeated four or five times in succession so that the residual gas from the preceding fillings was small.

At the outset of the experiment the carbon monoxide was allowed to remain in the chamber for several days without any data being taken. This served to remove such impurities as might gradually diffuse into the chamber from the walls. When readings finally were taken, it was found that the results were not altered by allowing the gas to remain in the chamber for twenty-four hours, and since the set of readings taken on one filling of gas in no case extended over a period of more than twelve hours, any effect due to contamination from the walls was negligible.

In the early part of this work the method of procedure in making the measurements was similar to that used in the original experiments. The mobility, determined by using the Rutherford square wave alternating potential method, now came out as high as 800 cm/sec/volt/cm at atmospheric pressure. However, with these high values for the mobility and with the limited range of frequencies obtainable with a commutator, the intercept of the mobility curve on the voltage axis was only one or two volts so that an error of a fraction of a volt in determining this intercept would alter the results appreciably.

In order to obtain frequencies such that the voltage intercepts of the mobility curves could be obtained as a function of the frequency for a much greater range of frequencies, the commutator was replaced by a vacuum tube oscillating circuit of the Hartley type, Fig. 1. For frequencies below 80,000 cycles, a high frequency transformer *T* was included in the plate circuit and the alternating potential was obtained from the secondary of this. For higher frequencies, since the transformer failed to transmit them, it was removed and the alternating potentials were obtained from the condenser *C* in the oscillating circuit. Results obtained in this way for frequencies below 80,000 cycles checked those obtained when the transformer was used.

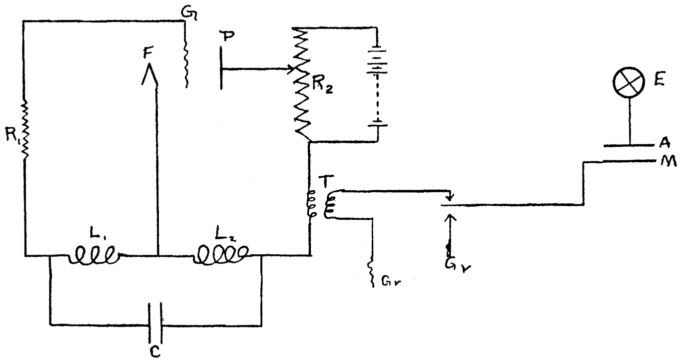

Fig. 1

One side of the secondary of the transformer was grounded and the other side was connected through a charge and discharge key to the brass plate *M* which together with the brass plate *A* was contained in the measuring chamber. The distance between *M* and *A* was 16 mm. The electrons were obtained photoelectrically from the plate *M*. In order to minimize the photoelectric emission from the plate *A* due to scattered light, this plate was coated with a layer of copper oxide by immersing it in an ammoniacal solution of copper carbonate and then heating the plate to redness in air. The alternating potential was varied by changing the potential of the plate *P* of the vacuum tube by means of the potential dividing rheostat R_2 and was measured by means of an electrostatic voltmeter. Then by noting the rate of deflection of the electrometer *E*, due to the charge received by *A* for various values of the alternating potential, mobility curves were obtained, and from the intercept of these curves on the voltage axis approximate values of the mobility were calculated from the relation

$$K = \frac{\pi n d^2}{\sqrt{2}\, v}, \qquad (1)$$

where d is the distance between the plated M and A, n is the frequency and v is the effective voltage of the intercept of the mobility curve, corrected for the change in potential of the plate A when a potential is applied to M.

Mobility curves were taken with intercepts ranging from 5 volts to 100 volts and at pressures ranging from 100 to 723 mm of mercury.

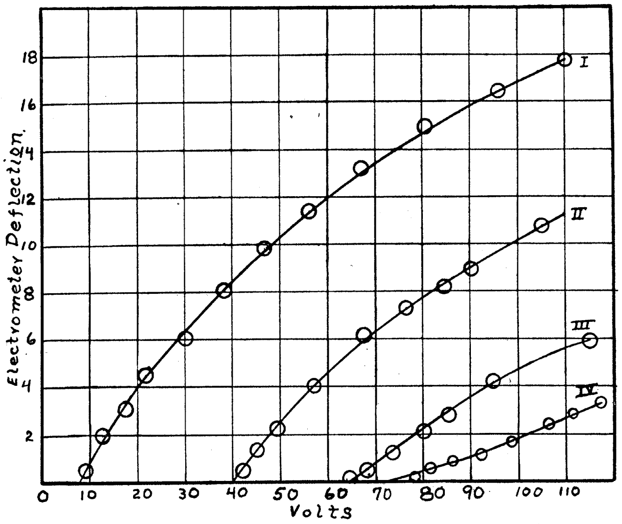

Fig. 2

Fig. 2 illustrates the types of curves obtained at a pressure of 723 mm for different frequencies. At the higher voltages (as may be seen from Curve IV.) the intercepts of these curves become less well defined and the curves show a tendency to approach the voltage axis asymptotically. Loeb[1] found the same thing to be true in his work on nitrogen and has suggested as a possible explanation that it might be due to the presence of impurities in the gas. If a small portion of the electrons become attached to molecules of the gas or impurity they would remain in the space between the plates and might under a space charge action gradually drift across to the upper plate. This effect disappeared in the case of carbon monoxide as the pressure was reduced, as might be expected on

---

[1] Leonard B. Loeb, Phys. Rev. (Jan., 1922).

the basis of Loeb's explanation, for the probability that an electron will become attached is then decreased.

The values of the mobility, for the curves of Fig. 2, as calculated from Eq. (1) are as follows:

Curve	v (corrected)	n	d	K
I.	7.2	15,030	16 mm	11,800
II.	38.0	63,025	" "	9,300
III.	61.7	94,340	" "	8,700
IV.	76.0	108,700	" "	8,150

It is to be noted that the mobility is higher for the low fields than for the high ones. For this reason values calculated on the basis of Eq. (1) must be considered as approximate only.

For the case of a sinusoidal alternating potential, Eq. (1) is derived from the expression

$$\frac{dy}{dt} = K\frac{V}{d}\sin 2\pi nt = KX\sin 2\pi nt = Kx, \qquad (2)$$

where dy/dt is the velocity of the electron in the direction of the field and x is the instantaneous value of the field intensity whose maximum is X. It is here assumed that K is independent of the field intensity and pressure. In the more general case where this is not so, Eq. (2) becomes

$$dy/dt = f(x, p)X \sin 2\pi nt.$$

For the case where the electrons just succeed in reaching the collecting plate during one half cycle of the alternating potential, that is for the case corresponding to the intercept of the mobility curve on the voltage axis, we get

$$d = \int_0^{\frac{1}{2n}} f(x, p)X_1 \sin 2\pi nt\, dt,$$

where X_1 is the value of the field corresponding to the intercept.

As may be seen from this equation, unless the form of the function $f(x, p)$ is known, an exact experimental determination of the mobility of the electron is impossible if a sine wave alternating potential is used.

Substituting for x its value in terms of X, placing $2\pi nt$ equal to θ and solving for n, we get

$$n = \frac{X_1}{2\pi d}\int_0^{\pi} f(p, X_1 \sin\theta)\sin\theta\, d\theta. \qquad (3)$$

From this we see that the form of the function must be such that the values of n calculated from this equation shall satisfy the experimental relations between n, X_1 and p.

Determination of $f(x, p)$.—Compton[1] has shown that if an electron loses a fraction q of its energy at each impact, the terminal energy W due to a field x is given by

$$W = 0.575\, xe\lambda/\sqrt{q}. \tag{4}$$

Furthermore, Townsend[2] gives as the expression for the mobility of an electron

$$K = .815\, e\lambda/m\bar{c}, \tag{5}$$

where λ is the mean free path and $\bar{c}$ is the mean velocity of agitation of the electrons. This velocity will be made up of two parts, first, that due to the velocity of agitation in equilibrium with the molecules when the field is zero, and second, the velocity of agitation due to the energy gained in the field. Applying this condition and combining Eqs. (4) and (5) Loeb[3] has shown that the mobility of the electrons should be given by the expression

$$K = .815 \frac{e\lambda}{m\bar{c}\sqrt{1 + .575xe\lambda/mc^2\sqrt{q}}}, \tag{6}$$

where $\bar{c}$ now refers to the velocity of agitation in thermal equilibrium with the molecules when the field is zero.

If it is assumed that λ varies inversely as the pressure, this expression reduces to

$$K = \frac{a}{p\sqrt{B + (x/p)}}\,. \tag{7}$$

Substituting this in Eq. (3) we get

$$n = \frac{aX_1/p}{2\pi d}\int_0^\pi \frac{\sin\theta\, d\theta}{\sqrt{B + (X_1/p)\sin\theta}}\,.$$

This is an elliptic integral which on reduction gives

$$n = \frac{\sqrt{2}\, a\sqrt{X_1/p}}{\pi d}\{2E(k, \varphi) - F(k, \varphi)\}, \tag{8}$$

where $\varphi = \sin^{-1}\sqrt{\dfrac{X_1/p}{B + (X_1/p)}}$ and $k = \sqrt{\left(1 + \dfrac{B}{X_1/p}\right)\Big/ 2}\,.$

Since k cannot be greater than unity, this solution holds only for $X_1/p \geqq B$.

That Eq. (8) satisfies the experimental results in the case of carbon monoxide may be seen from Fig. 3, where n computed from this expression

---

[1] K. T. Compton, Phys. Rev. 11, p. 196 (1918).

[2] J. S. Townsend, Electricity in Gases, p. 180.

[3] Loeb, loc. cit.

is plotted against the effective values of X_1/p. For this curve a has the value 1.87 $(10)^6$ and B equals .005, when the pressure is in mm Hg. The circles represent the experimental relations between the frequency and the effective values of X_1/p determined from the voltage intercepts of the mobility curves. Except for the lowest values the agreement is quite close.

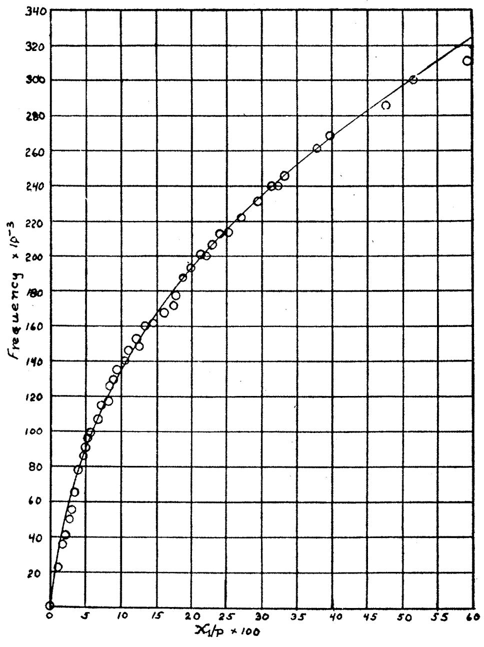

Fig. 3. Frequency as a function of X_1/p

Discussion of Results and Conclusions

The equation for the variation of the mobility of the electrons with field strength and pressure is, therefore, for carbon monoxide,

$$K = \frac{1.87\ (10)^6}{p\sqrt{.005 + (x/p)}} \cdot \tag{9}$$

This equation assumes that the electrons are in a steady state, that is that they have reached their terminal energy of agitation due to the field x. Actually such a steady state was probably never reached in these experiments due to the fact that the field in which the mobility was being measured was continually varying. However, the steady state condition would be approximated very closely if the fraction of the energy (q of Eq. 4) lost at each impact is large. Therefore since the Townsend-Compton equation for the mobility of an electron agrees with the data of these experiments, it seems reasonable to conclude that the collisions of an electron with the molecules of carbon monoxide are almost completely inelastic. Furthermore, indications are that q is constant; *i.e.*, the fraction of the energy lost at each impact is independent of the energy of the electrons at impact, over the range of energies reached in these experiments.

In the derivation of Eq. (7) from Eq. (6), the mean free path of the electron was assumed to be inversely proportional to the pressure and independent of the velocity of the electron. In general, this is not the case, as has been shown by Townsend,[1] Ramsauer[2] and Mayer.[3] For instance, in the case of nitrogen there is a large increase in the free path for low values of the electronic velocity. Apparently such a change does not exist in the case of carbon monoxide. However if the impacts are nearly inelastic, the energy of the electron would never become very great for the range of pressures and voltages used in these experiments so that a small variation of the free path of an electron with velocity would not be noticeable.

Because of the electronegative character of oxygen it might be expected that carbon monoxide would show a considerable affinity for electrons. The high values obtained for the mobility show that this is not so and that if the electrons unite with the molecules at all they do so very rarely.

UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN,
November 17, 1922

---

[1] J. S. Townsend, Phil. Mag. (Dec., 1921).
[2] Carl Ramsauer, Ann. der Phys. **66**, p. 546 (1921).
[3] H. F. Mayer, Ann. der Phys. **64**, p. 451 (1921).